Microchannel Steam Reformation of Hydrocarbon Fuels

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Objectives

- Evaluate the increase in productivity of steam reforming at temperatures greater than 650°C.
- Evaluate increase in sulfur tolerance at temperatures >650°C.
- Design and build low-pressure drop reactor, vaporizer and air recuperator that can maintain efficiency while exhibiting very low air side pressure drop.
- Test rapid start strategy for steam reforming reactor and associated heat exchangers.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-Up/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency

Approach

- Assemble high temperature reforming components including an Inconel 625 reactor and recuperator to allow testing of microchannel steam reforming at reformate outlet temperatures >650°C.
- Measure reforming capacity as a function of temperature for methane, isooctane and benchmark fuel at ~1 kWe scale. Evaluate capacity at conversion levels of ~99.9% and >99.995% (no detectable non-methane hydrocarbons).
- Evaluate reformer performance with up to 30 ppmw sulfur in the fuel.
- Design and build low pressure drop microchannel reactors and associated heat exchangers to enable testing of an approach to rapid startup.
- Perform initial testing of the rapid start approach.

Accomplishments

- Completed measurement of reformer capacity vs. temperature above 650°C for reforming methane, isooctane and benchmark fuel.
- Measured productivity vs. temperature above 650°C while reforming benchmark fuel with no detectable non-methane hydrocarbons in the reformate (conversion > 99.995%).
- Completed preliminary testing using sulfur spikes.
- Completed initial testing of combustor (atomized gasoline) to provide heat to fast-start system.

- Microchannel components for low pressure drop reforming system (reactors, water vaporizer, air recuperator, reformate recuperator) are designed and fabricated through the diffusion bonding step.

Future Directions

- Continue sulfur tolerance and carbon formation testing at elevated temperatures.
- Evaluate reforming performance of low pressure drop reactor design.
- Evaluate a potentially improved (lower-cost, increased durability) reforming catalyst which is now available.
- Evaluate fast-start approach using stainless steel fast-start components.
- Once data collection for high temperature sulfur tolerance and carbon deposition testing is complete, revise fast-start design to utilize smaller, lighter high-temperature reformer.
- Integrate fast start reformer system with water gas shift (WGS) and preferential oxidation (PrOx) reactors at 2 kWe scale.

Introduction

This project is applying the rapid heat and mass transfer attainable in microchannels to the development of a highly compact and efficient steam reformer. Once developed, the steam reformer will fit on-board a highly efficient fuel cell vehicle and provide hydrogen to a proton exchange membrane (PEM) fuel cell, which in turn will produce electricity to power the vehicle. By reforming to produce hydrogen on-board the vehicle, the fuel can be gasoline, providing vehicle range, and the need to purify and compress hydrogen is eliminated. Also, an automobile with on-board reforming could be fueled using the existing gasoline infrastructure, an important advantage if a hydrogen refueling infrastructure is not available.

In past work, this project demonstrated that steam reforming, normally considered a slow reaction, can achieve rapid kinetics in a microchannel reactor. In addition, it was demonstrated that this technology could be scaled up (10-25 kWe equivalent) and that the reforming reactor along with an integrated network of highly efficient microchannel heat exchangers could be highly compact and yet efficient. An approach to build water vaporizers having very low air side pressure drops was developed and demonstrated. A water vaporizer using this design sized for a 50-kWe fuel processor was delivered to McDermott as part of a fuel processing demonstration. Evaluation of microchannel reforming data indicated significant increases in reformer capacity might be available at higher temperatures than initially tested. The potential increase was judged to be sufficient in magnitude that the reduction in reactor mass might justify use of higher-priced alloys in place of stainless steel. In addition, the reactor tolerance for sulfur, a contaminant found in gasoline which must be removed prior to the PEM fuel cell, was expected to improve at higher temperature. Reforming the fuel and removing the sulfur from reformate is expected to be easier than removing the sulfur from liquid fuel. The current work examines the extent to which the reformer productivity and sulfur tolerance improve at temperatures above 650°C. In addition, work to develop a rapid-start capability, critical for an on-board automotive application, is being pursued (an earlier prototype required ~15 minutes for a cold start). The effort is aimed at assembling and testing a steam reforming system including the reformer and its associated heat exchangers that can cold start within ~30 seconds. Once demonstrated, the system will be expanded to include the WGS and PrOx reactors.

Approach

Reforming Capacity at High Temperature - The testing of reforming productivity was performed on an ~1 kWe test stand which has been shown to relate well to performance obtained in larger scale reactors. The reforming reactor shown in Figure 1 was integrated into a system of heat exchangers and tested at temperatures above 650°C. In a typical reforming test, the temperature and flow of the combustion stream were held constant. The feed rates of hydrocarbon and steam were then increased (or decreased) while maintaining a fixed 3:1 steam to carbon ratio until there was a small but easily measurable residual of non-methane hydrocarbon in the reformate. For isooctane and benchmark fuel, this translated to a conversion level of 99.7% to 99.9%. When reforming methane, the approach to equilibrium methane content was used, and the approach was 96% to 99%. After operating at each point for sufficient time to assure short-term stability, the combustion side temperature was changed and flows readjusted to obtain another point on the productivity vs. temperature curve. After completing the curve for benchmark fuel, an additional curve was generated in which the flows were reduced until there were no detectable non-methane hydrocarbons in the reformate (>99.995% conversion).

Sulfur Tolerance at High Temperature - The same reactor and test system used for the productivity vs. temperature experiments is now being used to test the sulfur tolerance at temperatures above 650°C. Sulfur spikes equivalent to 30 ppmw sulfur in the liquid fuel are being introduced by adding H2S to the vaporized fuel and steam and by spiking the liquid fuel with benzo-thiophene and thiophene.

Fast Start Reformer - Calculations were performed to define a steam reforming system, including the reforming reactor and associated heat exchangers, which would be able to start up within 30 seconds. The design is based on maintaining a very low pressure drop through the heat exchangers and reactors. During startup, the combustion gases flow through the reactors and vaporizer in parallel so that the high air flow does not result in a high pressure drop. The flow during normal operation is then changed to pass through reactors in series to reduce the total air flow and maintain efficiency. The low pressure drop during the startup period results in the fan required to provide the air flow being relatively less expensive. In addition, the electrical power requirement is low enough to be within the reach of a conventional automotive battery. The low pressure drop during normal operation reduces the cost of the fan but, perhaps more importantly, significantly reduces the parasitic power associated with air compression compared to either a steam reformer with higher pressure drops or an autothermal reformer operating at multiple psi pressures.

Results

Reforming Productivity vs. Temperature - The test reactor used to explore high temperature reforming rates is shown with the reformate recuperator and combustor attached to it in Figure 1. Reforming results are shown in Figure 2. Dramatic increases in processing rate were observed as the reformate outlet temperature was increased from 650°C to 875°C. The reforming rate of benchmark fuel increases exponentially as temperature is increased with no indication of leveling off due to heat or mass transfer limitations. This translates into the potential to significantly reduce reactor size if reforming at higher temperature.

Sulfur Tolerance vs. Temperature - Preliminary results of the improvement in sulfur tolerance with increased temperature are shown in Figure 3. Reforming at a temperature of 800°C or more significantly increases the ability of the catalyst to

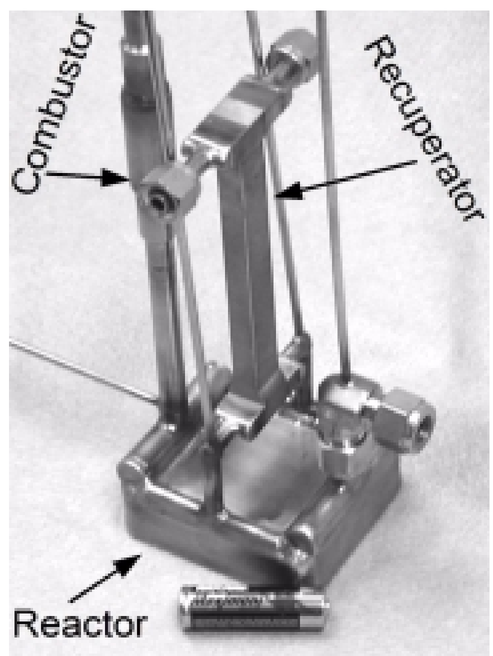

Figure 1. Inconel 625 Reactor Used for High Temperature Steam Reforming Tests (Reformate recuperator and combustor are shown attached.)

process the sulfur containing fuel without losing activity. Additional testing with spikes up to 30 ppmw S in the fuel introduced as hydrogen sulfide (added as gas to vaporized steam/fuel), thiophene and benzothiophene have confirmed the ability of the catalyst to process this level of sulfur with moderate reduction in activity for short periods of time. However, an increase in pressure drop over time across the reactor when reforming sulfur-spiked benchmark fuel has been observed. The increase in pressure drop is halted if the spike is removed. It is believed that this is an interaction between the high-nickel alloy Inconel 625 used to fabricate the high temperature reformer and the sulfur content in the fuel. This issue is being investigated further.

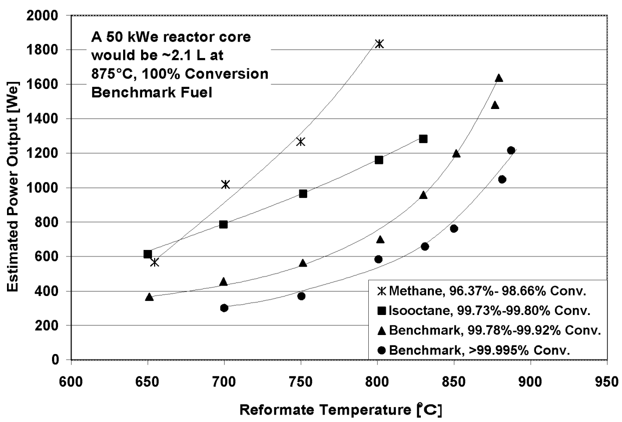

Figure 2. Throughput of Inconel 625 Reactor as a Function of Reformate Outlet Temperature (Throughput is expressed as electrical output. This could support assuming 90% conversion of CO in a WGS reactor, 50% selectivity in a PrOx reactor and a PEM fuel cell operating at 44% efficiency.)

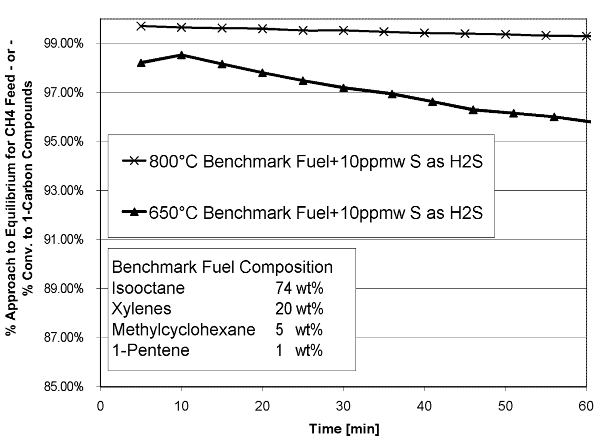

Figure 3. Increase in Sulfur Tolerance While Reforming Benchmark Fuel at 800°C vs. 650°C

Fast Start Reformer - The microchannel hardware required for testing the rapid start approach has been designed, and individual components have been fabricated through the diffusion bonding step. The microchannel components are shown in Figure 4. During normal operation, the 2-kWe system will require about 100 slpm of air flow with a pressure drop of 6.0 inches of water. During startup the system will utilize ~4000 slpm at a pressure drop of 5.2 inches of water. The pressure drop is maintained low by routing combustion gases in parallel through components during the startup period. A startup combustor was tested and demonstrated to provide the required flow of 800°C combustion gas in ~2 seconds.

Conclusions

- The exponential gain in steam reformer productivity with temperature while reforming benchmark fuel implies a reactor operating at 850°C can be less than 1/3 the size of a reactor operating at 650°C.

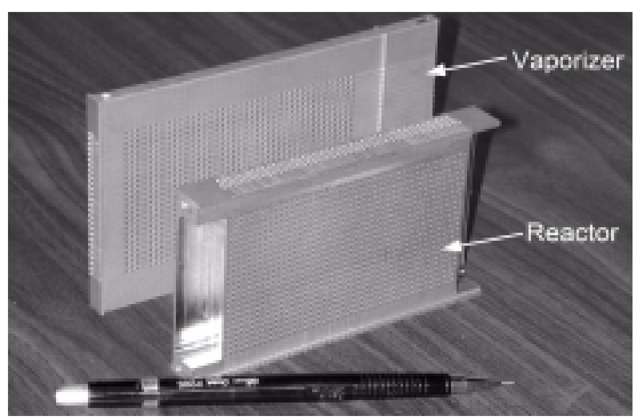

Figure 4. Low Pressure Drop Reactor System Components to be Used in Rapid Start Testing (The reactor weighs 400 g and supports ~500 We at 650°C. If produced in high temperature alloy and operated >850°C, the reactor would be capable of 2 kWe. The vaporizer weighs 325 grams and supplies steam for 2 kWe reforming capacity.)

- The steam reformer can provide reformate with no detectable non-methane hydrocarbons over the temperature range tested.
- The sulfur tolerance of the catalyst is significantly improved by operating at temperatures >800°C.
- The addition of a sulfur to benchmark fuel resulted in increases in pressure drop over time across the Inconel 625 steam reformer. This is being investigated.
- The approach to achieving rapid start of the steam reformer appears feasible.

FY 2003 Publications/Presentations

1. Whyatt, G. A., K. Brooks, J. Davis, C. Fisher, D. King, L. Pederson, S. Stenkamp, W. Tegrotenhuis, B. Wegeng. Progress in Microchannel Steam Reformation of Hydrocarbon Fuels. Presented at the Hydrogen, Fuel Cells and Infrastructure Technologies Program 2003 Merit Review and Peer Evaluation Meeting, May 19-22, 2003 Berkeley CA.

Special Recognitions & Awards/Patents Issued

1. Patent Application: System for Rapid Cold Startup of Microchannel Steam Reformer. #60-471,286, G. A. Whyatt.